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(54) **Method for making an article with shape-memory properties and some of the thus obtained articles.**

(57) Object of the invention is a method for making an article with shape-memory properties comprising the steps of heating a composition comprising at least one block copolymer, said composition characterized by at least two thermal transition temperatures, one of said transition temperatures being a predetermined lower transition temperature in the range of 20°C to 62°C, the other of said transition temperatures being an upper transition temperature above 62°C, said composition further characterized by the physical properties of a polymer selected from the group consisting of rigid, crystalline polymers and rigid, glassy polymers, below said predetermined lower transition temperature and the physical properties of a flexible, rubbery polymer at and above said predetermined lower transition temperature but below said upper transition temperature, to a temperature above said upper transition temperature, orienting said composition under stress into a first configuration, cooling said composition to below said predetermined lower transition temperature while said composition is in said first configuration, and cold forming said composition into a second configuration, as well as some of the thus obtained articles.

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# METHOD FOR MAKING AN ARTICLE WITH SHAPE-MEMORY PROPERTIES AND SOME OF THE THUS OBTAINED ARTICLES

Generally, the present invention relates to a method for making an article with shape memory properties using a composition that softens at a predetermined or selected temperature between approximately room temperature and approximately 62° C (about 25° C above body temperature) but maintains good mechanical integrity well above that softening point. The present invention also relates to biomedical devices and materials and articles with shape-memory properties made by this process.

The used composition is ideally suited for biomedical uses and is especially suited for catheters. Because catheters are inserted into the body, the ideal catheter should have a high flexural modulus or stiffness similar to that of a hypodermic needle. This is particularly true for intravenous catheters which are inserted through the skin for a short distance and then inserted directly into a blood vessel. Since ease of insertion is a property that is most important in initially placing the catheter, intravenous catheters have always been made from high flexural modulus materials. Once the catheter is in place inside the vein, the stiff property or high flexural modulus is a distinct disadvantage. High flexural modulus can result in irritation of the inner surface of the blood vessel by the tip of the catheter. As a result of the inflammatory irritation to the inside of the blood vessel, it is very common for these catheters to produce blood clots and become infected.

A very soft, rubber-like material would have much less tendency to irritate the inside of the blood vessel and would result in reduced morbidity and increased life of the catheter (the length of time before the catheter has to be replaced or moved to a different site). However, a flexible catheter would lack ease of insertion. Thus, there is a need for a catheter which is both easy to insert and does not irritate the inside of the blood vessel. The ideal catheter composition would have a very high modulus or stiffness upon insertion and would soften once inside the blood vessel.

It is an object of the present invention to provide a process using compositions that soften at a predetermined or selected temperature between approximately room temperature and approximately 62° C (about 25° C above body temperature) but maintain good mechanical integrity above that softening point, and the method of making said composition.

It is another object of the present invention to provide articles with shape memory properties that soften at predetermined temperatures between 20° C and 62° C.

Accordingly, the object of the invention is a method for making an article with shape-memory properties comprising the steps of heating a composition comprising at least one block copolymer, said composition characterized by at least two thermal transition temperatures, one of said transition temperatures being a predetermined lower transition temperature in the range of 20° C to 62° C, the other of said transition temperatures being an upper transition temperature above 62° C, said composition further characterized by the physical properties of a polymer selected from the group consisting of rigid, crystalline polymers and rigid, glassy polymers, below said predetermined lower transition temperature and the physical properties of a flexible, rubbery polymer at and above said predetermined lower transition temperature but below said upper transition temperature, to a temperature above said upper transition temperature, orienting said composition under stress into a first configuration, cooling said composition to below said predetermined lower transition temperature while said composition is in said first configuration, and cold forming said composition into a second configuration.

According to a preferred embodiment said composition is in the dry state at below said predetermined lower transition temperature in which said composition is characterized by the physical properties of a polymer selected from the group consisting of rigid, crystalline polymers and rigid, glassy polymers, and said composition is in the hydrated state at above said predetermined lower transition temperature to 62° C in which said composition is characterized by the physical properties of a flexible, rubbery polymer.

Particularly preferred is the use of a composition which further comprises a plasticizer selected from the group consisting of polyvinylchloride, styreneacrylonitrile copolymers, polyhydroxyethers, polycarbonates, polyesters, polyethers, nitrocellulose, cellulose derivatives and polystyrene.

More preferred is the fact that the block copolymer is selected from the group consisting of block copolymers having a polyester block, block copolymers having a polyether block, and polyurethane/ureas.

Specially preferred is a polyester-polyether.

According to a variation said block copolymer comprises polyester urethane and said plasticizer comprises phenoxy resin or the block copolymer comprises a polyester-polyether and said plasticizer comprises phenoxy resin.

The used composition should comprise 30 to 70 weight percent of said phenoxy resin and 70 to 30

weight percent of said polyester-ether.

It is still preferred that the transition temperature is at about body temperature and said first configuration is a catheter or a drug-release device or a thermal indicator.

The predetermined glass transition temperature should be in the range of from 10°C above body temperature to 62°C.

Finally, the object of the invention is a toy or a component of a toy with shape-memory properties as obtained by the above-mentioned process, whereby said toy component is in particular doll hair.

In one embodiment the composition comprises at least one block or segmented copolymer having a lower thermal transition temperature (T<sub>g</sub>) or a melting point (T<sub>m</sub>) between 20°C and 62°C and an upper thermal transition temperature (either a T<sub>g</sub> or T<sub>m</sub>) above 62°C. A major volume fraction of the block copolymer should have a lower transition temperature between 20°C to 62°C to ensure the necessary drop in flexural modulus when the composition passes through the lower transition temperature. The major volume fraction of the block copolymer must also have the physical properties of a rigid, glassy or crystalline polymer below the lower transition temperature and the physical properties of a flexible, rubbery polymer at and above the lower transition temperature but below the upper transition temperature.

In another embodiment of the present invention, the used composition comprises at least one block copolymer and a material that is selected from the group consisting of plasticizers and polymers that are thermodynamically compatible with at least one block of said block copolymer. Other blocks or segments of the block copolymer base are thermodynamically incompatible with the plasticizer or second polymer. The plasticizer or second polymer has at least one thermal transition temperature, (either a T<sub>g</sub> or T<sub>m</sub>) and the block copolymer base has at least two thermal transition temperatures.

The block copolymer or segmented copolymer is the base polymer of the composition. The plasticizer or second polymer is blended together with the base polymer. The compatible blocks of the base polymer and the plasticizer or second polymer form a miscible blend with a transition temperature between the thermal transition temperature of the compatible block of the base polymer and the thermal transition temperature of the plasticizer or second polymer. The transition temperature of the miscible blend may be varied by varying the relative amounts of the two components. The blocks or segments of the base polymer which are incompatible with the plasticizer or second polymer should have a T<sub>g</sub> or T<sub>m</sub> higher than the temperature range to be encountered in the end use of the composition of the present invention. The incompatible block of the base polymer will have a T<sub>g</sub> or T<sub>m</sub> in the composition very close or equal to the T<sub>g</sub> or T<sub>m</sub> it had in the unblended base polymer.

At temperatures above the predetermined transition temperature of the used composition, the blend will be analogous to a thermoplastic elastomer with a soft block transition temperature that may be varied over a wide range of temperatures. The temperature range over which the transition takes place will narrow if the two miscible components are highly compatible, producing an abrupt change in the mechanical, thermal, transport, electrical, and other properties of the blend as the temperature is raised or lowered through the transition temperature.

The properties of the blend at temperatures above and below the predetermined transition temperature can be varied considerably by varying the composition of the base polymer. Greater concentration of the miscible or compatible block in the base polymer will result in a greater proportion of the blend subsequently possessing the predetermined transition temperature of the composition. For instance, in a 60/40 blend of a polycaprolactone(PCL)/diisocyanatodiphenylmethane(MDI)/butanediol(BD) polyurethane base polymer and phenoxy resin, the soft block PCL concentration of the base polymer may be varied. At very low PCL concentration, the blend will be very rigid below the predetermined transition temperature and will soften little when heated above the predetermined transition temperature. At high PCL concentration in the base polymer, the blend will soften dramatically above the predetermined transition temperature.

Similarly, the incompatible blocks or segments of the base polymer may be chosen to vary the properties of the blend. A hard block composed of hexamethylenediisocyanate and butanediol would have a lower transition temperature than a rigid block of diisocyanatodiphenylmethane and butanediol within the range of end use temperatures.

The compatible block or blocks in the base polymer and the second polymer or plasticizer have special requirements relative to each other. In addition to being thermodynamically compatible as determined by a single transition temperature for the blend, the block copolymer (base polymer) and plasticizer or second polymer are selected such that the lower transition temperature (T<sub>g</sub> or T<sub>m</sub>) of the block copolymer is different than the transition temperature (T<sub>g</sub> or T<sub>m</sub>) of the plasticizer or second polymer, one of the transition temperatures being higher and one lower than the desired or predetermined transition temperature of the composition. Generally, the compatible block of the base polymer will have the lower T<sub>g</sub> or T<sub>m</sub> and the second polymer will have the higher T<sub>g</sub> or T<sub>m</sub>. As the second polymer is added to the base

polymer, the  $T_g$  or  $T_m$  of the soft block or segment of the base polymer increases. However, it is also possible to use a higher  $T_g$  or  $T_m$  base polymer with two hard blocks only one of which is compatible with the lower  $T_g$  or  $T_m$  plasticizer. As the lower  $T_g$  or  $T_m$  plasticizer or second polymer is added to the base polymer, the  $T_g$  or  $T_m$  of the compatible block of the base polymer decreases. In both cases, the relative amount of the second polymer or plasticizer will determine the final  $T_g$  or  $T_m$  of the compatible block of the base polymer and accordingly, the predetermined thermal transition temperature of the blend.

The composition used in the present invention is further characterized by the physical properties of a rigid, glassy, semi-crystalline, or crystalline polymer below the predetermined transition temperature and the physical properties of a soft, rubbery polymer at and above the predetermined transition temperature, but below the upper transition temperature of the composition. The physical or mechanical properties of glassy or crystalline polymers and rubbery polymers are described in "Mechanical Properties of Polymers and Composites," L.E. Nielsen, Dekker, N.Y. (1974), and "Properties of Polymers, Their Estimation and Correlation with Chemical Structure," D. W. Van Krevelen, Elsevier, N.Y. (1976), and are well known to those skilled in the art.

For biomedical uses, a preferred embodiment of the composition used in the present invention has a predetermined glass transition temperature between body temperature and  $62^\circ\text{C}$ . For certain biomedical applications, such as making catheters, drug release devices, or thermal indicators, a preferred embodiment of the composition has a glass transition temperature at or near body temperature.

Accordingly, for certain biomedical applications, a preferred embodiment of the composition used in the present invention is characterized by the physical properties of a rigid, glassy or crystalline polymer in the dry state at a temperature below body temperature (preferably at a temperature between  $25 - 35^\circ\text{C}$  or below) and is characterized by the physical properties of a flexible, rubbery polymer in the hydrated state at about body temperature to the next transition temperature which should be above at least  $50^\circ\text{C}$ , preferably above  $62^\circ\text{C}$ .

For biomedical applications, a preferred composition used in the present invention comprises at least one block copolymer and a second polymer thermodynamically compatible with at least one block of said block copolymer, wherein the block copolymer is characterized by at least two thermal transition temperatures, one being below body temperature and the other being well above body temperature, preferably above  $62^\circ\text{C}$ . The second polymer has at least one transition temperature (either a  $T_g$  or  $T_m$ ) above body temperature.

The block copolymer (base polymer) is selected from the group consisting of polyester urethanes, polyether urethanes, polyurethane/ureas, polyether polyamides, polyether polyesters, and any other block or segmented copolymers containing at least one polyether or polyester block or segment. One preferred block copolymer (base polymer) is a polyester urethane. Polyester urethanes have glass transition temperatures of  $-50^\circ\text{C}$  to  $-10^\circ\text{C}$  and  $100^\circ\text{C}$  to  $150^\circ\text{C}$ . Another preferred block copolymer is a polyether urethane. Polyether urethanes have glass transition temperatures of  $-85^\circ\text{C}$  to  $-40^\circ\text{C}$  and  $100^\circ\text{C}$  to  $150^\circ\text{C}$ .

The second polymer is preferably selected from the group consisting of polyvinylchloride, styrene/acrylonitrile copolymers, polyhydroxyethers, polycarbonates, polyesters, polyethers, nitrocellulose, cellulose derivatives, and polystyrene. A preferred second polymer is the polyhydroxyether of bisphenol-A and epichlorohydrin (phenoxy resin). The phenoxy resin has a glass transition temperature of  $98^\circ\text{C}$ . The two polymers are then blended in a ratio so that the predetermined lower transition temperature for the composition will be at or near body temperature or slightly above body temperature if hydration lowers this glass transition temperature further.

When used for catheters or other biomedical applications, the composition may also contain a minor amount of a surface modifying additive. The surface modifying additive reduces the coefficient of friction and increases blood compatibility of the composition. In addition, radiopaque fillers may be used in the composition to render the catheters visible by fluoroscopy. Surface modifying additives may be selected from the group consisting of block/segmented multipolymers containing polysiloxanes or polyfluorocarbons as one block. Preferred surface modifiers are selected from the group consisting of polysiloxane/polyester block copolymers and polysiloxane/polyurethane copolymers. A more preferred surface modifier is a polysiloxane/polyester block copolymer. Radiopaque fillers may be selected from the group consisting of barium sulphate, bismuth sub-carbonate, bismuth oxychloride, tantalum and other non-corrosive metals. A preferred radiopaque filler is barium sulphate.

For use as a catheter, a preferred embodiment of the used composition has a glass transition temperature at or near body temperature, such that when the composition is at room temperature, it is below its glass transition temperature and is stiff and rigid, having the physical properties of a glassy or crystalline polymer. Accordingly, a catheter made of the composition will be easy to insert through the skin and not the blood vessel. As the composition warms to body temperature, it will go through the transition

and its flexural modulus will be decreased by about one to three orders of magnitude, causing the composition to soften considerably. Thus, while in the blood vessel the catheter will have less tendency to irritate the inside of the blood vessel and thus, less tendency to cause blood clots and become infected.

Because most intravenous catheters have thin walls, they have a tendency to heat up very quickly when exposed to a new temperature. As a result, the catheter can actually begin to soften as it is being inserted into the body, making insertion difficult. Therefore, a more preferred embodiment of the composition of the present invention has a predetermined lower thermal transition temperature slightly above body temperature. When the catheter is inserted into the body, the composition absorbs water from the blood and becomes plasticized; its predetermined lower transition temperature is lowered from slightly above body temperature to just below body temperature. The composition then goes through its transition to become a rubbery, flexible solid.

Another use for the composition is for making contact lenses that soften at or near body temperature in the hydrated state. At room temperature, the composition would have a high flexural modulus and therefore could easily be machined into lenses. Once put in place in the eye, the composition would heat up, absorb water, pass through its predetermined lower transition temperature and become soft, flexible, and comfortable for the wearer and more permeable to gases, such as oxygen and carbon dioxide.

For other biomedical applications, a preferred embodiment of the composition used according to the present invention will have a predetermined lower transition temperature above body temperature but below 62°C and an upper transition temperature above 62°C, such that the composition has the physical properties of a rigid, glassy or crystalline polymer at about body temperature and the physical properties of a flexible, rubbery polymer at 10°C above body temperature to just below the upper transition temperature.

An example of a biomedical use for this preferred embodiment of the composition of the present invention is for making a material for constructing casts for broken limbs. The composition can be formed into a biomedical tape which can be softened by warming it to its predetermined lower transition temperature in hot or warm water or with a heat gun. When it becomes soft and flexible, it can be used to wrap a broken limb that has just been set. As the material cools to room temperature, it goes through the lower transition and becomes virtually as rigid as Plaster of Paris. The material remains rigid at body temperature to at least bathing temperature. The composition may replace Plaster of Paris as a material for constructing casts.

Another variation of the present invention is for making articles with shape-memory properties that change shapes at a predetermined transition temperature in the range of about 25°C to about 62°C. For example, the composition can be heated to a temperature above its upper transition temperature, oriented under stress into a specific shape (configuration #1) then cooled while in that configuration #1 to below the lower predetermined or selected transition temperature of the composition. The composition can then be cold formed into another shape (configuration #2) at that temperature. When the composition is heated to a temperature above the lower predetermined transition temperature but below the upper transition temperature, it will spontaneously reassume configuration #1.

Thus, for instance, a catheter with shape-memory properties could be made from the composition of the present invention. The composition could be formed into a catheter in one configuration above its upper transition temperature then cooled to below a lower transition temperature at or near body temperature and formed into a second configuration (e.g., a straight configuration). Upon insertion into the body, the catheter would warm to body temperature (its lower glass transition temperature) and reassume its first configuration.

Another use for the composition of the present invention would be for the production of toys with shape-memory properties. The composition could be oriented under stress into one toy shape above the composition's upper transition temperature. When cooled below the predetermined lower transition temperature, the toy could be reshaped by children. Then, the toy could be warmed to above its predetermined lower transition temperature, thus reassuming its original shape.

The various blocks or segments of the block copolymer are selected such that the physical properties of the composition are that of a rigid, glassy or crystalline polymer below the predetermined lower transition temperature of the composition and that of a flexible, rubbery polymer at and above the lower transition temperature, but below the upper transition temperature.

The block copolymer selected for use in the composition of the present invention can be made by a method described in: 1. J. A. Moore, ed., *Macromolecular Syntheses*, Collective Vol. 1, John Wiley and Sons, N.Y., (1977), p. 79,381. 2. J. H. Saunders, and K.C. Frisch, eds., *Polyurethanes, Chemistry and Technology*, Vol. 1, Chemistry, Interscience Div. of John Wiley and Sons, N.Y., (1962). 3. W. R. Sorenson and T. W. Campbell, *Preparative Methods in Polymer Chemistry*, Interscience Div. of John Wiley and Sons, N.Y., (1961).

A second embodiment of the method comprises the steps of selecting the desired transition tempera-

ture for the composition, selecting or making a block copolymer such that said block copolymer has at least two thermal transition temperatures. The lower transition temperature of the block copolymer should be either above or below the predetermined or selected lower transition temperature of the composition. A plasticizer or second polymer that is thermodynamically compatible with at least one block of the block copolymer and that has at least one thermal transition temperature (either a  $T_g$  or  $T_m$ ) that is either above or below the predetermined transition temperature of the composition is selected or prepared, then blended together with the block copolymer such that the lower thermal transition temperature of the block copolymer and the thermal transition temperature of the compatible plasticizer or second polymer combine to form the predetermined lower transition temperature of the composition. The plasticizer selected for use in the composition of the present invention can be made by the method described in W. R. Sorenson and T. W. Campbell, Preparative Methods in Polymer Chemistry, Interscience Div. of John Wiley and Sons, N.Y., (1961), and G. Odian, Principles of Polymerization, McGraw-Hill, N.Y. (1970). The second polymer selected for use in the composition of the present invention can be made by the method described in W. F. Hale, Encyclopedia of Polymer Science and Technology, 10,111 (1969), and H. Lee, D. Stoffey, and K. Neville, New Linear Polymers, McGraw-Hill, N.Y., (1967).

For biomedical uses, a surface modifier and/or a radi-opaque filler can be blended together with the block copolymer in the first embodiment of the method of the present invention or with the base polymer and thermodynamically compatible plasticizer or second polymer in the second embodiment of the method.

The present invention also contemplates a method of making biomedical devices or materials that soften at a predetermined or selected temperature between body temperature and  $62^{\circ}\text{C}$ . In most applications, the predetermined softening temperature will be at or near body temperature. The method comprises the steps of making the necessary composition by either of the method embodiments discussed above, then forming it into a biomedical device or material. This composition can be formed into a catheter, a drug release device, a thermal indicator, biomedical tape for constructing casts for broken limbs, contact lenses or many other biomedical devices.

The following table indicates the decreasing flexural modulus of a preferred composition used in the present invention for biomedical uses when it comprises various ratios of phenoxy resin and polyester urethane:

	Phenoxy Resin/ Polyester Urethane Wt/Wt	Flexural Modulus [psi]		
		23°C Dry	37°C Dry	37°C Hydrated
35	60/40	186400	159000	6729
	50/50	160400	8950	602
	40/60	93300	2867	1186

The flexural modulus data in the column designated "37°C Hydrated" was obtained by measuring the composition's flexural modulus after one hour of hydration in  $37^{\circ}\text{C}$  distilled water. The flexural modulus data in the two columns designated "Dry" was obtained by measuring the composition in its dry state at the designated temperatures. The following examples describe the tests from which this data was obtained and the preferred compositions of the present invention.

#### Example 1

A composition comprising 60 weight percent of a resin comprised of the polyhydroxyether derived from bisphenol-A and epichlorohydrin (phenoxy resin) and 40 weight percent of a commercial polyester urethane (Estane 5707 produced by B.F. Goodrich), in the form of compression molded sheets, was measured for flexural modulus in a thermal mechanical analyzer at  $23^{\circ}\text{C}$ ,  $37^{\circ}\text{C}$  and at  $37^{\circ}\text{C}$  after an hour of hydration in distilled water. The flexural modulus of the composition at  $23^{\circ}\text{C}$  was 186,400. The flexural modulus at  $37^{\circ}\text{C}$  was 159,000 and the flexural modulus after one hour of hydration in  $37^{\circ}\text{C}$  distilled water was 6,729.

#### Example 2

A composition comprising 50 weight percent of the phenoxy resin described in Example 1 and 50 weight percent of the polyester urethane described in Example 1, in the form of compression molded sheets, was measured for flexural modulus in a thermal mechanical analyzer. At 23 °C, the composition had a flexural modulus of 160,400. At 37 °C, the composition had a flexural modulus of 8,950 and after one hour of hydration in 37 °C distilled water, the composition had a flexural modulus of 602.

Transition temperatures of each blend component separately and of the final composition were measured by differential scanning calorimetry (DSC) as follows:

Phenoxy resin:  $T_g = 91^{\circ}\text{C}$   
 Polyester urethane:  $T_g = -19^{\circ}\text{C}$   
 Blend (50% phenoxy resin/50% Estane 5707):  $T_g = 39^{\circ}\text{C}$

Additionally, 40 weight percent of the phenoxy resin, 40 weight percent of the polyester urethane, and 20 weight percent of a polysiloxane-polycaprolactone block copolymer surface modifier (36 weight percent polysiloxane) were melt blended. The transition near body temperature of that composition as measured by DSC was  $T_g = 27^{\circ}\text{C}$ .

#### Example 3

A composition comprising 40 weight percent of the phenoxy resin described in Example 1 and 60 weight percent of the polyester urethane described in Example 1, in the form of compression molded sheets, was measured for flexural modulus in a thermal mechanical analyzer. At 23 °C, the composition had a flexural modulus of 93,300. At 37 °C, the composition had a flexural modulus of 2,867 and after one hour of hydration in 37 °C distilled water, the composition had a flexural modulus of 1186.

#### Example 4

A composition comprising 50 weight percent of the phenoxy resin described in Example 1 and 50 weight percent of a commercial polyether-based polyurethane (Estane 5714 produced by B.F. Goodrich) were melt blended and the transition temperatures were measured by differential scanning calorimetry (DSC) as follows:

Phenoxy resin:  $T_g = 91^{\circ}\text{C}$   
 Polyether-based polyurethane:  $T_g = -48^{\circ}\text{C}$   
 Blend (50% phenoxy resin/50% polyurethane):  $T_g = 22^{\circ}\text{C}$

Additionally, 40 weight percent of the phenoxy resin, 40 weight percent of the polyether-based polyurethane, and 20 weight percent of a polydimethylsiloxane-polycaprolactone block copolymer surface modifier (36 weight percent polysiloxane) were melt blended. The transition temperature occurring around but below body temperature as measured by DSC was  $T_g = 5^{\circ}\text{C}$ . This result indicates that the selected surface modifier is thermodynamically compatible with the base polymer and the second polymer. Less surface modifier should be used to achieve a final  $T_g$  near 22 °C. Typically for biomedical applications, about 0.5 weight percent of a surface modifier would be used.

#### Claims

1. A method for making an article with shape-memory properties comprising the steps of heating a composition comprising at least one block copolymer, said composition characterized by at least two thermal transition temperatures, one of said transition temperatures being a predetermined lower

transition temperature in the range of 20 °C to 62 °C, the other of said transition temperatures being an upper transition temperature above 62 °C, said composition further characterized by the physical properties of a polymer selected from the group consisting of rigid, crystalline polymers and rigid, glassy polymers, below said predetermined lower transition temperature and the physical properties of a flexible, rubbery polymer at and above said predetermined lower transition temperature but below said upper transition temperature, to a temperature above said upper transition temperature, orienting said composition under stress into a first configuration, cooling said composition to below said predetermined lower transition temperature while said composition is in said first configuration, and cold forming said composition into a second configuration.

2. A method according to Claim 1, wherein said composition is in the dry state at below said predetermined lower transition temperature in which said composition is characterized by the physical properties of a polymer selected from the group consisting of rigid, crystalline polymers and rigid, glassy polymers, and said composition is in the hydrated state at above said predetermined lower transition temperature to 62 °C in which said composition is characterized by the physical properties of a flexible, rubbery polymer.
3. A method according to Claim 1, wherein said composition further comprises a plasticizer selected from the group consisting of polyvinylchloride, styreneacrylonitrile copolymers, polyhydroxylethers, polycarbonates, polyesters, polyethers, nitrocellulose, cellulose derivatives and polystyrene.
4. A method according to one of the preceding claims, wherein said block copolymer is selected from the group consisting of block copolymers having a polyester block, block copolymers having a polyether block, and polyurethane/ ureas.
5. A method according to Claim 4, wherein said block copolymer comprises a polyester-polyether.
6. A method according to Claim 4, wherein said block copolymer comprises polyester urethane and said plasticizer comprises phenoxy resin.
7. A method according to Claim 4, wherein said block copolymer comprises a polyester-polyether and said plasticizer comprises phenoxy resin.
8. A method according to Claim 7, wherein said composition comprises 30 to 70 weight percent of said phenoxy resin and 70 to 30 weight percent of said polyester-ether.
9. A method according to Claim 1, wherein said predetermined transition temperature is at about body temperature and said first configuration is a catheter.
10. A method according to Claim 1, wherein said predetermined transition temperature is at about body temperature and said first configuration is a drug-release device.
11. A method according to Claim 1, wherein said predetermined transition temperature is at about body temperature and said first configuration is a thermal indicator.
12. A method according to Claim 1, wherein said predetermined glass transition temperature is in the range of from 10 °C above body temperature to 62 °C.
13. A toy or component of a toy with shape-memory properties made by the method of Claim 1.
14. A toy component according to Claim 13 comprising doll hair.



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(54) **Method for making an article with shape-memory properties and some of the thus obtained articles.**

(57) Object of the invention is a method for making an article with shape-memory properties comprising the steps of heating a composition comprising at least one block copolymer, said composition characterized by at least two thermal transition temperatures, one of said transition temperatures being a predetermined lower transition temperature in the range of 20°C to 62°C, the other of said transition temperatures being an upper transition temperature above 62°C, said composition further characterized by the physical properties of a polymer selected from the group consisting of rigid, crystalline polymers and rigid, glassy polymers, below said predetermined lower transition temperature and the physical properties of a flexible, rubbery polymer at and above said predetermined lower transition tem-

perature but below said upper transition temperature, to a temperature above said upper transition temperature, orienting said composition under stress into a first configuration, cooling said composition to below said predetermined lower transition temperature while said composition is in said first configuration, and cold forming said composition into a second configuration, as well as some of the thus obtained articles.

**EP 0 422 693 A3**



European  
Patent Office

## EUROPEAN SEARCH REPORT

Application Number

EP 90 12 3938

### DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	US-A-4 193 899 (D. BRENNER et al.) * Claims 1,2,4,11; column 6, line 3 - column 7, line 31; column 8, line 30 - column 9, line 14; column 10, lines 3-68 * - - - -	1	C 08 L 75/04 C 08 L 71/00 C 08 L 67/00 A 61 L 29/00
X	US-A-3 619 455 (I.T. CLEMENT et al.) * Claims 1,8,10; column 2, lines 15-50 * - - - -	1	A 61 K 9/22 A 63 H 3/44 B 29 C 61/00 //
A	EP-A-0 087 329 (LABORATOIRES D'HYGIENE) * Claims 1,17,18; page 6, line 28 - page 7, line 6; page 7, example 1; page 10, lines 12-29 * - - - -	1,3,4,12	(C 08 L 75/04 C 08 L 71:00 ) (C 08 L 71/00 C 08 L 75:04 ) (C 08 L 71/00 C 08 L 67:00 ) (C 08 L 67/00 C 08 L 71:00 )
X	US-A-4 473 671 (R. GREEN) * Claim 1; column 3, line 33 - column 4, line 20; column 7, line 21 - column 8, line 19 * - - - -	1,4,12	
A	US-A-4 053 548 (R.D. LUNDBERG) * Claim 1; column 1, lines 6-19 * - - - -	1	
A	EP-A-0 129 396 (HOWMEDICA INC.) * Claim 1; page 5, lines 1-6; page 7, lines 11-19 * - - - -	1	
A	FR-A-2 546 170 (AKZO) * Claims 1,14,15; page 6, line 35 - page 7, line 6 * - - - -	1	
A	US-A-3 384 679 (T.T. STETZ) * Claim 1; column 4, lines 20-35 * - - - -	1,4,6	
A	DE-A-1 704 160 (KABEL- UND METALLWERKE) * Claims 1,2; page 2, paragraphs 1-3 * - - - - -	1	
The present search report has been drawn up for all claims			
Place of search		Date of completion of search	Examiner
The Hague		22 April 91	VAN PUYMBROECK M.A.
<b>CATEGORY OF CITED DOCUMENTS</b>			
X: particularly relevant if taken alone		E: earlier patent document, but published on, or after the filing date	
Y: particularly relevant if combined with another document of the same category		D: document cited in the application	
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P: intermediate document			
T: theory or principle underlying the invention		&: member of the same patent family, corresponding document	